

EVALUATION OF STABLE ISOTOPES AND SOLUTE GEOCHEMISTRY FOR DETERMINING SOURCES OF DISSOLVED SULFATE IN GROUNDWATER¹

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Abstract. Stable isotope data for sulfur ($\delta^{34}\text{S}_{\text{SO}_4}$) and oxygen ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) were used in conjunction with dissolved solute data to distinguish between sulfate derived from mine wastes and sulfate from geothermal discharge in alluvial groundwater within the southern Deer Lodge Valley, Montana. Sulfate plumes in the valley are present in groundwater down-gradient of impounded mill tailings. Also, geothermal water with comparable sulfate concentrations discharges locally to groundwater. The distribution and mass of sulfate in groundwater has been used to assess the degree of mining related impacts to groundwater in the area without recognizing sulfate contributed by geothermal sources. In this study, solute and isotope chemistry were evaluated and used to estimate the extent to which geothermal water contributes to the overall mass of sulfate in groundwater. It is estimated that less than 10 percent of the total mass of sulfate in the shallow groundwater system is derived from geothermal discharge.

Additional Key Words: Mine waste, groundwater quality, geothermal discharge, isotopic signatures, graphical analyses

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Introduction

The southern Deer Lodge Valley encompasses approximately 130 square miles in west-central Montana. Trending north-south, the valley is about thirty-two miles long and averages approximately ten miles in width. The city of Anaconda, Montana is situated in the western perimeter of the study area and Butte, Montana lies approximately nine miles to the southeast (Figure 1). The southern Deer Lodge Valley is the southern portion of the larger Deer Lodge Basin and is surrounded by the Flint Creek Range to the west and the Anaconda-Pintlar Range and Pioneer Mountains to the south. Peaks in the surrounding mountains typically rise to between 8,000 and 9,500 feet with the exception of Mt. Haggin in the Anaconda-Pintlar Range, which reaches an altitude of 10,665 feet above sea level. The continental divide lies about 5 to 15 miles east of and roughly parallel to the valley axis. Silver Bow Creek flows north through the center of the southern half of the study area. The Clark Fork River is formed at the confluence of Silver Bow and Warm Springs Creeks. Four other perennial streams flow eastward into the valley: Willow Creek, Mill Creek, Lost Creek, and Modesty Creek. Several ephemeral streams enter the site from the east (Figure 2). The valley floor drops from about 5,140 feet above sea level where Silver Bow Creek crosses the southern study area boundary to about 4,700 feet at the point where the Clark Fork River exits the northern boundary of the study area.

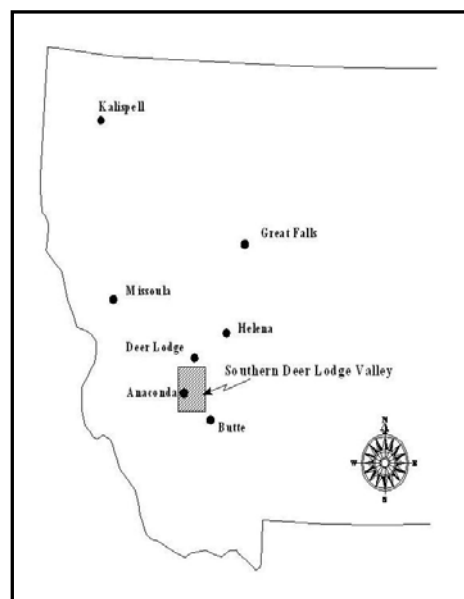


Figure 1: Study Area Location

The valley has been impacted on a large scale by historic mining and smelting activity in Butte and Anaconda. Butte is a world renowned mining district with nearly continuous production of copper and other metallic ores from 1864 to the present. Anaconda was the home of the Washoe Smelter and Reduction Works, facilities built and operated by the Anaconda Copper Company to process copper ore mined in Butte. The Washoe Works were situated on Smelter Hill, just east of town, and operated from 1902 until it was closed in 1980. As a result of mining activity in Butte and ore-processing operations in Anaconda, millions of tons of mining-related wastes remain in designated impoundments and intermixed with surficial soils and fluvial sediments throughout the southern Deer Lodge Valley. Wastes produced by smelting activities at the Washoe Reduction Works include mill and concentrator tailings, flue dust, furnace slag, and smelter fall-out. More than 200 million cubic yards of tailings generated at the Washoe Reduction Works are present in the Anaconda and Opportunity Tailings Ponds (Atlantic Richfield, 1996). Also, large volumes of tailings and contaminated sediments carried downstream from Butte are deposited as channel and overbank deposits along Silver Bow Creek and in the Warm Springs Treatment Ponds just upstream from the Clark Fork River headwaters.

Oxidation processes acting upon metal-sulfide minerals contained in the waste materials result in the release of sulfate and trace elements to groundwater. Analyses of groundwater samples show elevated concentrations of arsenic, cadmium, copper, iron, manganese, zinc, and sulfate, frequently at levels exceeding federal primary and/or secondary drinking water maximum contaminant levels. In general, elevated trace element concentrations are observed in close proximity to known mining-related source areas, but sulfate is more widespread (Figure 2).

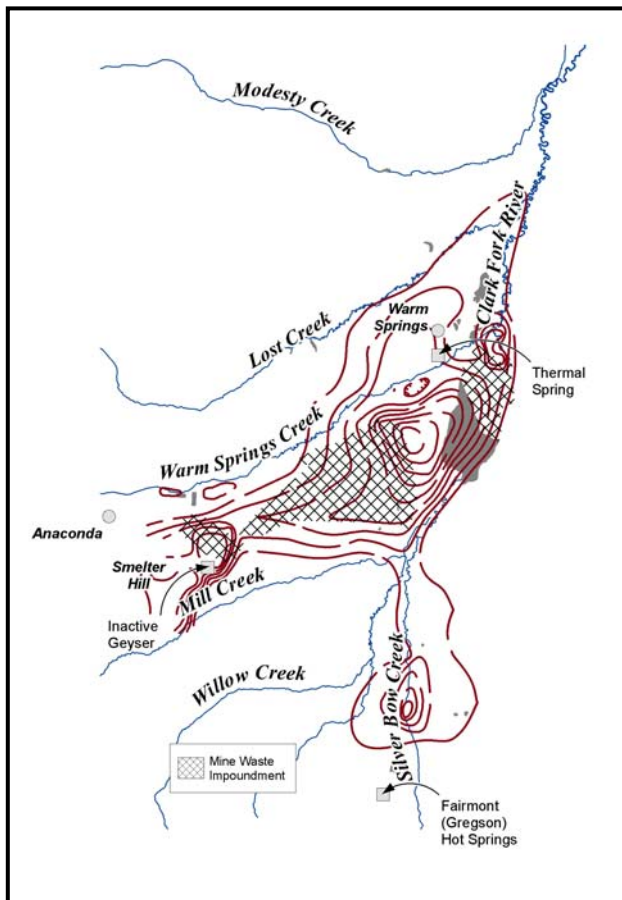


Figure 2: Sulfate isoconcentration map for shallow alluvial groundwater in the southern Deer Lodge Valley

Dissolved sulfate is present in groundwater at concentrations that range from below 10 milligrams per liter (mg/L) to more than 2,000 mg/L. The highest levels of sulfate are observed in groundwater on Smelter Hill and immediately down-gradient of the Anaconda, Opportunity, and Warm Springs Ponds. Although waste materials are undoubtedly a major source of sulfate, the elevated sulfate levels in groundwater cannot be attributed completely to anthropogenic sources. Sulfate-rich geothermal water discharges from two thermal springs in the valley, an inactive geyser, and two surface seeps on Smelter Hill. The geothermal water may enter the shallow groundwater system along deep-seated basin-forming fault zones. The concentration of dissolved sulfate in the thermal water varies from one discharge point to the next (180 mg/L to 1,360 mg/L), but is within the range of sulfate concentrations observed in groundwater in the valley.

Sulfate in groundwater within the southern Deer Lodge Valley originates from leaching of sulfidic mining-related wastes and geothermal discharge. These sources may be distinguished by their isotopic and major ion compositions. Solute concentrations are high in both waters (total dissolved solids [TDS] > 500 mg/L), but thermal waters are enriched in the heavy isotope of sulfur (^{34}S) and depleted in the heavy isotope of oxygen (^{18}O) with respect to mine-waste leachate. Also, pure geothermal water characteristically has a higher percentage of sodium than mine-waste leachate. This study examines isotopic and solute geochemistry

to estimate the relative contributions of dissolved sulfate to the alluvial groundwater system from geothermal discharge and from leaching of mining and smelting wastes.

Study Approach

Available groundwater chemistry data were evaluated and sorted according to compositional similarities, geographic location, and site-specific hydrogeologic conditions. Sources of dissolved sulfate were investigated. Isotopic and major ion chemistry was evaluated for geothermal and mining-related source areas. Extensive graphical analysis was performed to determine end-member compositions for geothermal and mining-related waters and interpret mixing relationships in groundwater. Based upon the sulfate concentration and estimated rate of discharge for geothermal and mining-impacted waters, as well as the established groundwater mixing relationships, the relative sulfate contributions from both geothermal and mining-related sources to the shallow alluvial groundwater system were estimated.

Geology and Hydrogeology

The southern Deer Lodge Valley is a north-trending structural basin bounded to the west by normal faults and filled with several thousand feet of sediment (valley fill) eroded from rocks in the surrounding mountains. East of the valley, the mountains are composed chiefly of Cretaceous granite (Boulder Batholith). West of the valley, the Flint Creek and Anaconda-Pintlar ranges consist of folded and faulted complexes of Precambrian metasedimentary rocks (Belt) and Paleozoic and Mesozoic sedimentary rocks that have been intruded by granitic masses (McLeod, 1987). Mountains south of the study area are composed chiefly of Tertiary volcanics, Cretaceous plutonic rocks, and Precambrian gneiss.

Major Cenozoic normal faults block out discrete basins in the Deer Lodge Basin that generally become deeper to the north. In the southern Deer Lodge Valley, Cenozoic normal faults are present along the western margin of the valley as far south as Smelter Hill in Anaconda. The fault bounding the east side of the graben may be antithetic with respect to the valley margin fault on the west. If projected southward, the trace of the eastern fault extends beneath the town of Warm Springs, and may continue farther south beneath Fairmont Hot Springs. A series of southwest-northeast directed normal faults may cross-cut the valley between Mill Creek and Lost Creek, dropping the valley progressively deeper to the north. The presence of this cross-valley fault system may explain the strikingly parallel trends of Mill Creek, Warm Springs Creek, and Lost Creek. Also, the presence of cross-valley faults are useful for explaining the locations of geothermal springs on Smelter Hill and Warm Springs.

Within the study area, groundwater exists in unconsolidated Quaternary and Tertiary alluvium. Groundwater also occurs in fractured igneous, sedimentary, and metamorphic rocks of the surrounding highlands, but the permeability of these consolidated rocks is very low compared with the unconsolidated deposits within the

basin (Konizeski, 1968). The alluvial aquifer is a thick accumulation of valley fill sediments. Fill material consists of Quaternary glacial outwash, shallow Quaternary alluvium, and deeper alluvium which may be either Quaternary or Tertiary age. Quaternary glacial outwash consists of nearly homogeneous clean sand and gravel with frequent cobbles. Well logs indicate that the outwash materials are very coarse near the mouths of Warm Springs Creek, Mill Creek, and Lost Creek valleys, becoming finer toward the north and east. The Quaternary/Tertiary alluvium (deeper alluvium) consists of the entire spectrum of terrigenous sediments ranging from clay to gravel. Quaternary alluvium contains laterally discontinuous lenses of clay, and mixed silts, sands, and gravels. Stratigraphic horizons in the deeper alluvium are more obvious; often with relatively thick layers contiguous for thousands of square feet.

In general, the shape of the water table mimics topography within the study area, sloping toward the center of the valley and then swinging to the north under Silver Bow Creek and the Clark Fork River (Figure 3). Groundwater discharges to the streams at lower elevations within the valley. Groundwater throughout the southern portion of the study area is funneled toward Silver Bow Creek and the Clark Fork River. The alluvial aquifer south of Lost Creek and beneath the Clark Fork River is therefore vulnerable to chemical influences from all mining-related and geothermal source areas located to the south, including waste materials in the Anaconda, Opportunity, and Warm Springs Ponds, and geothermal discharge at Warm Springs, Fairmont Hot Springs, and Smelter Hill.

Groundwater in the alluvial aquifer exists under unconfined to semi-confined conditions. Unconfined conditions abound in Quaternary glacial outwash, but semi-confining units (i.e., clay and silt) are present locally. This is particularly true in the deeper alluvium, where clay and silt units are typically thicker and more continuous than in the shallow Quaternary deposits. Groundwater recharge to the alluvial aquifer is provided from infiltration of precipitation, surface water infiltration, groundwater flux

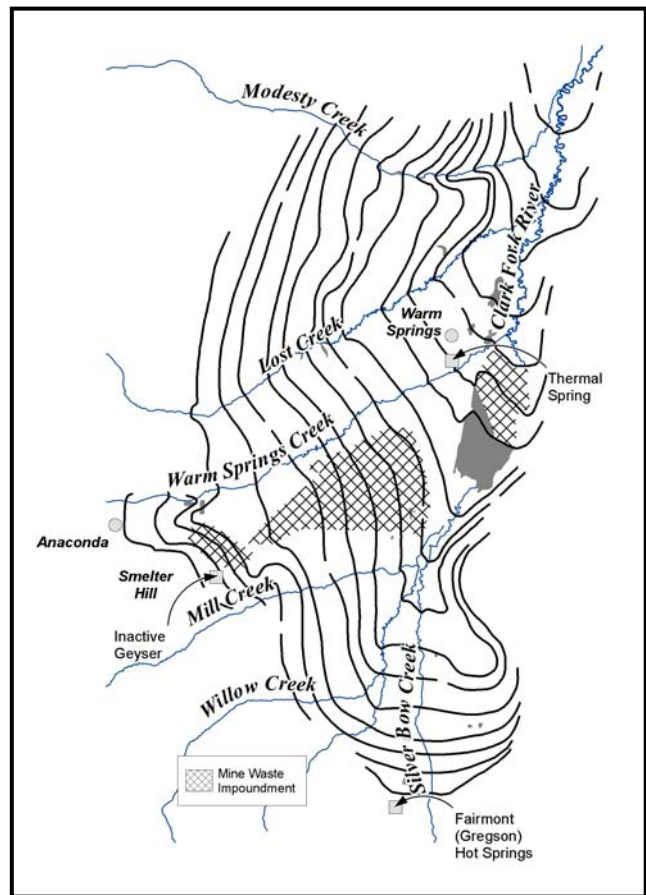


Figure 3: Potentiometric surface map of shallow alluvial groundwater in the southern Deer Lodge Valley

from tributary valleys, groundwater flux from the bedrock aquifer(s) along the valley margins and presumably at depth, and geothermal discharge.

Occurrence of Geothermal Water

Two geothermal springs are present in the southern Deer Lodge Valley. The first is located in Warm Springs on the campus of the Montana State Hospital. The second is located in Gregson at the Fairmont Hot Springs Resort, about 4 miles south of Opportunity. In addition, an inactive geyser and two springs/seeps on Smelter Hill discharge water with isotopic and chemical signatures indicative of geothermal influences.

The geothermal spring at Warm Springs has a large mound of calcium carbonate (travertine), having a diameter of roughly 70 to 80 feet and an elevation of approximately 40 feet above the valley floor. Geothermal water discharges from the top of the mound. The rate of surficial discharge is approximately 60 gallons per minute (gpm) and the water temperature consistently measures between 170°F and 175°F. A well drilled 1,350 feet northeast of the geothermal spring for geothermal exploration penetrated 1,498 feet of unconsolidated sand, gravel, silt, and clay before encountering granitic basement rock (Stoker, 1980). This well yields high temperature (151°F) geothermal water under flowing-artesian pressure. The chemistry of the well water is nearly identical to the geothermal springs at Warm Springs.

Geothermal water issues from two springs located at the Fairmont Hot Springs Resort. Geothermal water is used to heat concrete-lined swimming pools at the resort. Since 1984, geothermal water has been pumped from a 600 foot deep well located approximately 1/4 mile southeast of Fairmont Hot Springs Resort. The well was installed by the Montana Bureau of Mines and Geology in 1982 for geothermal exploration purposes (Test Well 1-28-82) and subsequently left to the resort for geothermal water production. Well water temperature ranges from 165 to 170 °F (personal communication with Vern Cook - Fairmont Hot Springs Resort maintenance supervisor, November 1998). In August 1974, when the hot springs were sampled by USGS, discharge from the springs was recorded at 40 gpm and water temperature was 158°F (Mariner et al., 1976).

The inactive geyser on Smelter Hill discharges moderately warm water (71°F) at a rate of approximately 3 gpm (Sonderegger et al., 1981). The geyser discharges to the ground surface through small travertine cones. The geyser is located on the upthrown (west) side of the valley-margin fault that cross-cuts Smelter Hill. The surface expression of the fault is concealed beneath a travertine deposit generated by geothermal activity on Smelter Hill. The travertine deposit unconformably overlies Tertiary sedimentary deposits on the east side of Smelter Hill and the down-thrown side of the fault. The geyser is situated in the approximate center of the travertine deposit and discharges from Tertiary volcanic rock of the Lowland Creek Formation. Hydraulic head measured for the geyser is above natural land surface and is considerably higher than local groundwater in the underlying aquifers. The artesian head associated with the inactive geyser suggests

that it is not hydraulically connected to shallow groundwater. Given its elevated temperature, the surrounding travertine deposit, and location relative to the fault, it is reasonable to expect that the geyser is hydraulically connected to the fault, and furthermore that the fault plane serves as a conduit for upward migration of deep-circulating geothermal groundwater.

Two springs on Smelter Hill show similar chemical trends to the inactive geysers and therefore have been included in this study. Consistent with the inactive geysers, the springs are located west of the basin-margin fault that bisects Smelter Hill and issue from volcanic rocks of the Lowland Creek Volcanics. One spring is located near the head of Walker Gulch, which drains the north side of Smelter Hill. The second spring is located due south of the inactive geysers, and may reflect the trace of the fault, just north of where it crosses the Mill Creek Valley. No hydraulic testing has been performed on these springs to determine if they are in hydraulic communication with the volcanic bedrock aquifer, the fault, or whether they represent perched groundwater. However, their water chemistry suggests a geothermal influence and probable connection to the fault.

Recharge from precipitation in surrounding highland areas travels to depth through a network of fractures, faults, and/or fissures, is heated, and then is transmitted back to the surface along fault surfaces within the valley. Intersecting faults are interpreted to exist beneath Warm Springs and possibly Smelter Hill, and these fault intersections are thought to facilitate the upward migration of geothermal waters. Geothermal discharge at Fairmont Hot springs is most likely controlled by fractures within the granitic rocks south, west, and potentially east of Gregson. A north-south directed fault inferred beneath Warm Springs may extend south beneath Fairmont Hot Springs.

Solute and Isotope Geochemistry

The chemistry of alluvial groundwater in the southern Deer Lodge Valley is predominantly derived from mineral dissolution of valley fill sediments and consolidated rocks of the surrounding highlands. Secondary chemical influences include sulfide oxidation in mining and smelter wastes and geothermal discharge. The majority of wastes are in the Anaconda, Opportunity, and Warm Springs Ponds and also in overbank tailing deposits along Silver Bow Creek. Less conspicuous scattered tailing deposits and soils contaminated by roughly 80 years of smelter fallout may be significant. Geothermal water discharges from two geothermal springs, one inactive geyser, and at least two seeps. Also, geothermal water discharges at depth along basin-forming fault zones. Geothermal water and leachate from metal sulfide wastes contribute sulfate to the alluvial groundwater system in the southern Deer Lodge Valley.

Table 1 depicts the chemistry indicative of geothermal water, mine waste impacted groundwater, and groundwater un-impacted by either geothermal discharge or mining-related wastes in the southern Deer Lodge Valley. The chemistry of alluvial groundwater is variable within the study area. In general, groundwater that has not been

impacted by mining-related wastes or geothermal discharge is a calcium-bicarbonate type water with a TDS concentration less than 300 mg/L, a sulfate concentration less than 30 mg/L, and very low or undetectable concentrations of trace elements. Groundwater that has been impacted by mining-related wastes and/or geothermal discharge generally has elevated sulfate and intermediate to high TDS. Arsenic and trace metal concentrations typically are elevated in groundwater impacted by mine wastes.

Solute Geochemistry

Major ion chemistry was evaluated for 90 wells and 5 springs. Concentrations and relative percentages of the major ions were compared to identify chemical signatures specific to different source areas (e.g., geothermal water and mining-impacted waters), and to gain insight about groundwater recharge areas and specific flow paths for different portions of the alluvial aquifer.

Geothermal discharge from the spring at Warm Springs and from the inactive geysers on Smelter Hill is a calcium-sodium-sulfate water with high TDS. At Warm Springs, geothermal water has TDS exceeding 1,250 mg/L with calcium and sodium constituting 58.6 and 27.9 percent of the cations, respectively, and sulfate comprising 76.3 percent of the anions, based on concentrations in milliequivalents per liter (meq/L). At Smelter Hill, TDS exceeds 2,000 mg/L and the major ion composition is similar to the Warm Springs geothermal water with calcium and sodium constituting 65.7 and 18.0 percent of the cations, respectively, and sulfate representing 79.0 percent of the anions. Geothermal water at Fairmont Hot Springs is a sodium-sulfate-bicarbonate water with sodium constituting 96.1 percent of the cations and sulfate and bicarbonate comprising 47.5 and 33.2 percent of the anions, respectively. The Fairmont Hot Springs geothermal water also has lower TDS (542 mg/L) than the geothermal waters at Warm Springs and Smelter Hill. The difference in major-ion chemistry at Fairmont Hot Springs reflects a different solution chemistry within the geothermal reservoir and along the flow path prior to discharge.

Alluvial groundwater within the study area is generally either calcium-sulfate or calcium-bicarbonate type water. Calcium is the predominant cation in all groundwater samples analyzed, typically constituting more than 60 percent of the cations. Magnesium constitutes between 10 and 30 percent of the cations in all but four of the samples, which are less than 10 percent. Potassium concentrations are low, never exceeding more than 3

Table 1. Examples of the Water Chemistry Typical of Mine-Waste Impacted Groundwater, Geothermal Water, and Un-impacted Groundwater in the Southern Deer Lodge Valley

Sample ID	Location	TDS (mg/L)	Major Ions (meq/L)							Trace Elements (μg/L)							Stable Isotope Composition		
			Ca	Mg	K	Na	HCO ₃	CO ₃	SO ₄	Cl	As	Cd	Cu	Fe	Mn	Zn	δ ³⁴ S(SO ₄) (CDT)	δ ¹⁸ O(H ₂ O) (SMOW)	δD(H ₂ O) (SMOW)
Unimpacted Groundwater																			
GS-18	Mill Creek	112	0.95	0.40	0.02	0.25	1.31	0.00	0.17	0.02	0.7	2.0 u	3.0	2.0 u	2.0 u	3.0	ND	ND	ND
MW-217d	Opportunity Ponds	148	1.30	0.47	0.03	0.27	1.41	0.00	0.48	0.14 u	1.3 u	2.2 u	2.2 u	35 u	43	6.0 u	15.7	-19.5	-143
MW-224	Warm Springs Ck	154	2.14	0.71	0.04	0.16	2.16	0.00	0.40	0.14 u	1.3 u	2.2 u	2.2 u	20 u	5.0 u	6.0 u	ND	ND	ND
MW-233	Mill Creek	132	1.33	0.57	0.02	0.22	1.36	0.00	0.56	0.14 u	2.8 u	2.2 u	3.0 u	28 u	4.0 u	13.0 u	ND	ND	ND
Mine Waste Impacted Water																			
C2AL	Smelter Hill	1,340	13.22	3.78	0.12	2.20	1.61	0.00	15.72	0.37	2,380	2.2 u	3.0	13,700	8,710	9,690	2.9	-18.6	-137
C-25	Crackerville	790	7.53	1.71	0.14	2.10	2.02	0.00	8.20	0.56	2.3	9.6	26.2	166	3,820	2,060	ND	ND	ND
MW-217s	Opportunity Ponds	1,420	17.47	1.06	0.12	0.28	2.75	0.00	16.49	0.14 u	269	2.2 u	6.0 u	24,500	4,540	110	1.8	-18.0	-136
MW-215	Opportunity Ponds	2,980	28.89	10.20	0.28	0.95	4.10	0.00	36.44	0.20	7.0	0.10	3.0 u	80,500	20,500	236	3.8	-16.4	-132
WSP-11s	Warm Sp Pond #1	1,581	18.81	6.19	0.35	1.32	3.77	0.00	16.45	0.34	33.0	6.0	31.0	29,400	18,100	747	ND	ND	ND
Geothermal Water																			
MSH-HS	Warm Springs	1,250	10.43	1.81	0.55	4.98	3.41	0.00	11.66	0.14 u	25.0	1.0 u	3.0 u	1,310	52	11.0 u	21.7	-20.4	-155
FHS	Fairmont	559	0.19	0.01 u	0.10	7.42	2.62	0.10	3.75	0.48	ND	10.0 u	10.0 u	20.0 u	20 u	10.0 u	15.8	-20.3	-151
SH HS	Smelter Hill	2,310	23.45	5.51	0.27	6.42	7.19	0.00	28.32	0.20	5.1	3.9 u	3.1 u	1,210	480	29 u	18.8	-20.1	-151

Notes: u = undetected at the reported concentration

ND = not determined

meq/L – milliequivalents per liter

µg/L – micrograms per liter

δ³⁴S(SO₄) (CDT) – Sulfur isotope composition of sulfate relative to sulfur in the Canyon Diablo Meteorite

δ¹⁸O(H₂O) (SMOW) – Oxygen isotope composition of water relative to standard mean ocean water

δD(H₂O) (SMOW) – hydrogen isotope composition relative to standard mean ocean water

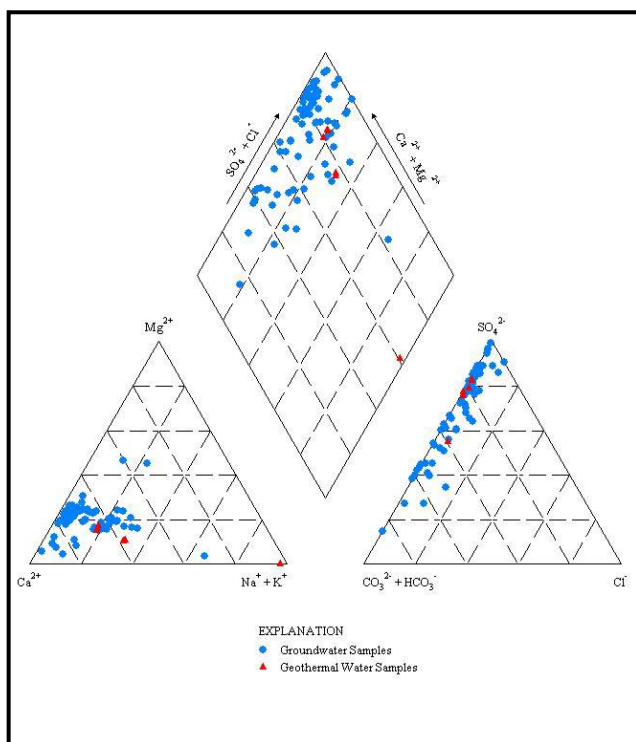


Figure 4: Trilinear plot for groundwater and geothermal water samples with total dissolved solids greater than 300 mg/L

Sulfate Distribution

Sulfate data were available for 124 monitoring wells, two geothermal springs (Warm Springs and Fairmont Hot Springs), one inactive geyser (SH HS), and two springs/seeps (SH-03 and SH-05). Concentrations of sulfate in groundwater range from below detection (5 mg/L) to 1,960 mg/L. The highest levels are observed in shallow wells along the toe of the Opportunity Ponds impoundment (800 - 1,960 mg/L). Sulfate concentrations are also significantly elevated at the toe of the Warm Springs Ponds (870-1,300 mg/L) and in the Tertiary alluvium on Smelter Hill (755 - 1,100 mg/L). The sulfate plume on Smelter Hill extends beneath and down-gradient from the toe of the Anaconda Ponds (695 - 911 mg/L). Sulfate concentrations observed in wells completed in shallow alluvium along Silver Bow Creek range from 56 mg/L to 394 mg/L. Concentrations measured in geothermal waters at Warm Springs, Smelter Hill, and Fairmont Hot Springs are 560 mg/L, 1,360 mg/L, and 180 mg/L, respectively. A sulfate isoconcentration map is presented in Figure 2.

Sulfate behaves conservatively in the aqueous environment, meaning that it is not readily attenuated by sorption processes or precipitation reactions. Consequently, sulfate is transported readily in groundwater. Comparing the shape of the contours depicted on the sulfate isoconcentration map with the potentiometric surface map indicates that sulfate moves in a down-gradient direction from the obvious source areas (i.e., Smelter

percent of the cations. Sodium constitutes less than 30 percent of the cations with the exception of 4 wells that range from 30 to 40 percent.

Sulfate and bicarbonate are the predominant anions in groundwater. The percentage of the anions varies with TDS, with sulfate comprising a greater percentage of the anions in groundwater with TDS greater than 300 mg/L (Figure 4). Geothermal waters discharging at Warm Springs and Smelter Hill have similar major ion chemistry to groundwater that has demonstrated impacts from leaching mine wastes. As previously indicated, low TDS (<300 mg/L) calcium-bicarbonate waters are indicative of groundwater that is not influenced by either mining related wastes or geothermal discharge (Figure 5).

Hill/Anaconda Ponds complex, Opportunity Ponds, and Warm Springs Ponds). An anomaly to this general pattern occurs north of Opportunity Ponds where the sulfate

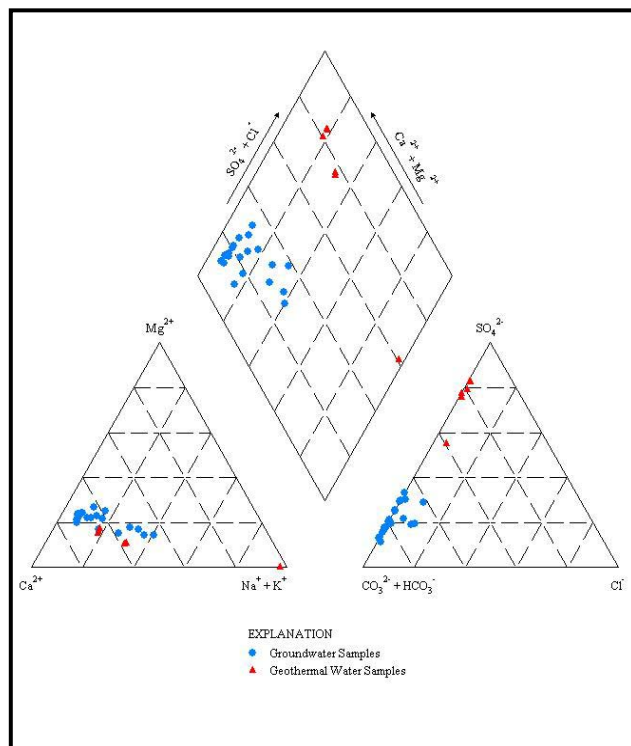


Figure 5: Trilinear plot for groundwater and geothermal water samples with total dissolved solids less than 300 mg/L

contours swing to the north across interpreted flow lines. It is also notable that sulfate concentrations are elevated above typical background (≤ 30 mg/L) in the southern part of the study area (north and east of Fairmont Hot Springs). These anomalies may be explained by different flow patterns for deeper groundwater and/or other sources of sulfate.

Trace Elements

Detectable and locally elevated concentrations of trace metals and arsenic occur in alluvial groundwater at specific locations in the southern Deer Lodge Valley. Concentrations of arsenic (As), iron (Fe), and manganese (Mn) in groundwater are significantly elevated beneath and immediately down-gradient of known mine waste impoundments and tailings deposits scattered along the Silver Bow Creek

floodplain). Cadmium (Cd), copper (Cu), and zinc (Zn) concentrations in alluvial groundwater are low and commonly below detection except for very localized plumes near major tailings accumulations. Trace metal concentrations in groundwater samples collected from wells located outside of a direct flow path from major waste sources are typically below detection. Concentrations of Cd, Cu, Fe, Mn, and Zn in the geothermal discharge at Fairmont Hot Springs are below detection and arsenic was not analyzed (Mariner et al., 1976; Leonard et al, 1978). Geothermal discharge at Warm Springs and Smelter Hill has notable concentrations of As (5 - 25 $\mu\text{g/L}$), Fe (1,210 - 1,310 $\mu\text{g/L}$), and Mn (52 - 480 $\mu\text{g/L}$), but Cd, Cu, and Zn were below detection. Thus, the distribution of trace metals and arsenic can be used to identify portions of the alluvial aquifer exhibiting obvious detrimental impacts imposed by mining-related wastes.

Isotopes

It is well established that stable isotopes of the same element differ in their physical and chemical properties and are fractionated (separated into light and heavy fractions) during naturally occurring chemical processes. Consequently, the measurement of the variations in their isotopes provides considerable insight concerning the origin and mode of formation of the minerals that contain them as well as the geologic and geochemical

processes to which they have been exposed. Most environmental isotope studies focus on these light elements and their isotopes: hydrogen (^1H , ^2H , ^3H), carbon (^{12}C , ^{13}C , ^{14}C), nitrogen (^{14}N , ^{15}N), oxygen (^{16}O , ^{18}O), and sulfur (^{32}S , ^{34}S).

Isotope effects are generally small and therefore fractional differences (δ) are expressed as the per mil (parts per thousand, ‰) difference of the ratio of the heavy isotope to the light isotope of the sample relative to a standard, defined as follows:

$$\delta_{\text{sample}} (\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

where R_{sample} represents isotope ratios of a sample ($^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$, $^{34}\text{S}/^{32}\text{S}$) and R_{standard} is the corresponding standard. The δ value for oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$), respectively, are calculated relative to standard mean ocean water (SMOW). SMOW represents an adequate isotope composition for “average ocean water” (Craig, 1961a). The accepted standard for sulfur is troilite (FeS) in the iron meteorite Canyon Diablo for which $^{34}\text{S}/^{32}\text{S}$ is assigned the value 1/22.22 (Thode, 1991).

In reference to groundwater studies, isotope fractionation can provide information regarding the origin of the groundwater itself, as well as the dissolved constituents which it bears. Isotope analyses for the hydrogen and oxygen isotope composition of water and for the sulfur isotope composition of dissolved sulfate were examined during this study. Isotope compositions provided valuable insight to the origins of the geothermal water and, in conjunction with dissolved solute concentrations, enabled chemical signatures to be identified for mining-impacted groundwater and for geothermal waters in the southern Deer Lodge Valley. Based upon the end-member chemistry of the respective waters, mixing relationships were established so that relative percentages of geothermally derived sulfate and mine-waste derived sulfate could be assigned to any and all groundwater data.

Hydrogen ($\delta^2\text{H}$) and Oxygen ($\delta^{18}\text{O}$). $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analyses were evaluated for 27 monitoring wells and 5 geothermal springs. The data are displayed in Figure 6 with respect to the meteoric water line for continental North America. The continental meteoric water line is defined as $\delta^2\text{H} = 7.95\delta^{18}\text{O} + 6.03\text{‰}$ (Gat, 1980) and is a derivative of the Global Meteoric Water Line ($\delta^2\text{H} = 8\delta^{18}\text{O} + 10\text{‰}$) established by Craig (1961b).

The distribution of the data is approximately that expected of meteoric waters in the Rocky Mountain Region (Savin, 1980) and furthermore, the data fall reasonably close to the trend of the meteoric water line, suggesting that both geothermal waters and groundwater are derived from precipitation. This suggests that geothermal discharge in the southern Deer Lodge Valley is the product of deep circulating meteoric waters and not the production of magmatic waters. This conclusion is consistent with that of Chadwick and Leonard (1979), who determined from chemical geothermometry that

normal geothermal gradients are sufficient to maintain the geothermal systems of southwestern Montana (including the southern Deer Lodge Valley) without enhancement from cooling igneous bodies.

Figure 6 illustrates that geothermal water is depleted in the heavy isotopes of hydrogen and oxygen relative to groundwater. On average, geothermal waters are depleted in ^{18}O by 1.8‰ and deuterium by 12.1‰. The depletion can be attributed to the relative difference in the altitude of the groundwater and geothermal system recharge areas. Typical ^{18}O and deuterium depletion gradients of 0.15-0.5‰ $\delta^{18}\text{O}$ /100 meters and 1.2-4‰ $\delta^2\text{H}$ /100 meters, respectively, may be expected. Based upon these gradients, the

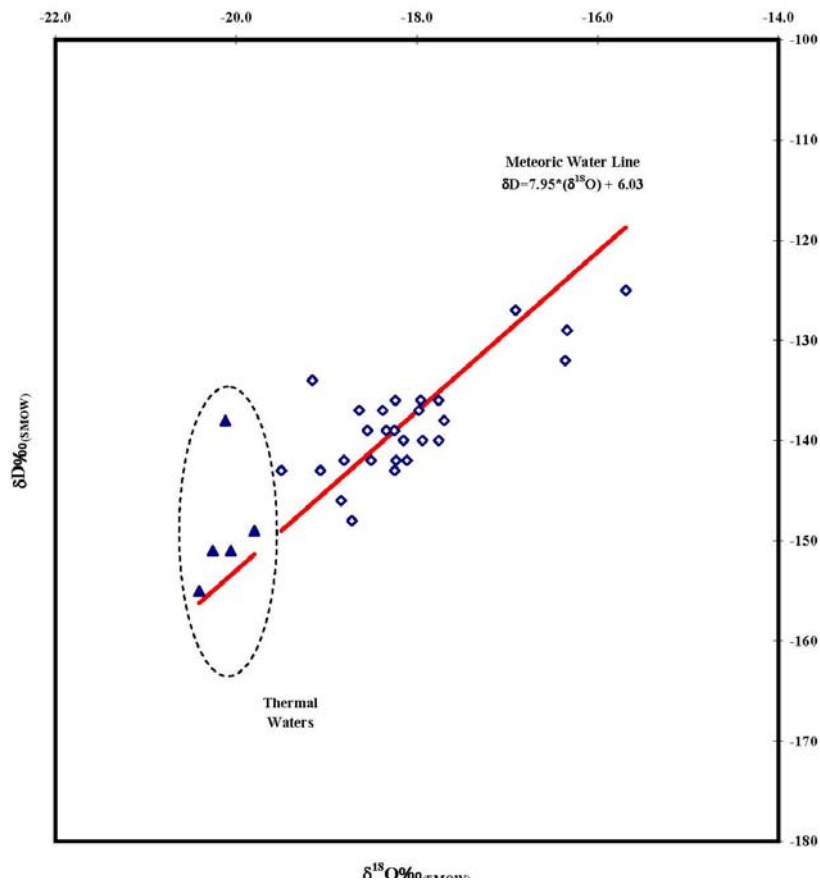


Figure 6: $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ vs. $\delta\text{D}_{\text{H}_2\text{O}}$ in groundwater and geothermal water.

recharge area for the geothermal system(s) in the southern Deer Lodge Valley is 300 to 1,200 meters higher than that for the groundwater. This would suggest that the geothermal recharge occurs in the mountains surrounding the valley whereas, groundwater recharge occurs predominantly from local infiltration.

Sulfur ($\delta^{34}\text{S}$)

Sulfur isotope data for sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) are available for 33 groundwater wells and 5 springs. $\delta^{34}\text{S}_{\text{SO}_4}$ values range from +2 to +21.8‰. The sulfur isotope composition of sulfate in geothermal water is enriched in ^{34}S relative to groundwater and ranges from +15.8 to +21.8‰. When $\delta^{34}\text{S}_{\text{SO}_4}$ is plotted against $\delta^{18}\text{O}$ (Figure 7), geothermal water is easily differentiated from groundwater as geothermal water is enriched in ^{34}S and depleted in ^{18}O relative to groundwater. The geothermal spring at Fairmont Hot Springs (FHS) has the lowest $\delta^{34}\text{S}_{\text{SO}_4}$ value determined for geothermal water (+15.8‰). $\delta^{34}\text{S}$ values determined from the inactive geyser (SH HS) and two springs on Smelter Hill (SH03 and SH05) range from +18.4 to +19.7‰. The sulfur isotope composition of sulfate determined for a geothermal spring (MSH HS) and a deep geothermal well (MSH TW) at Warm Springs were +21.6 ‰ and +21.8‰, respectively. $\delta^{34}\text{S}_{\text{SO}_4}$ values in groundwater range from +1.8 to +21.3‰.

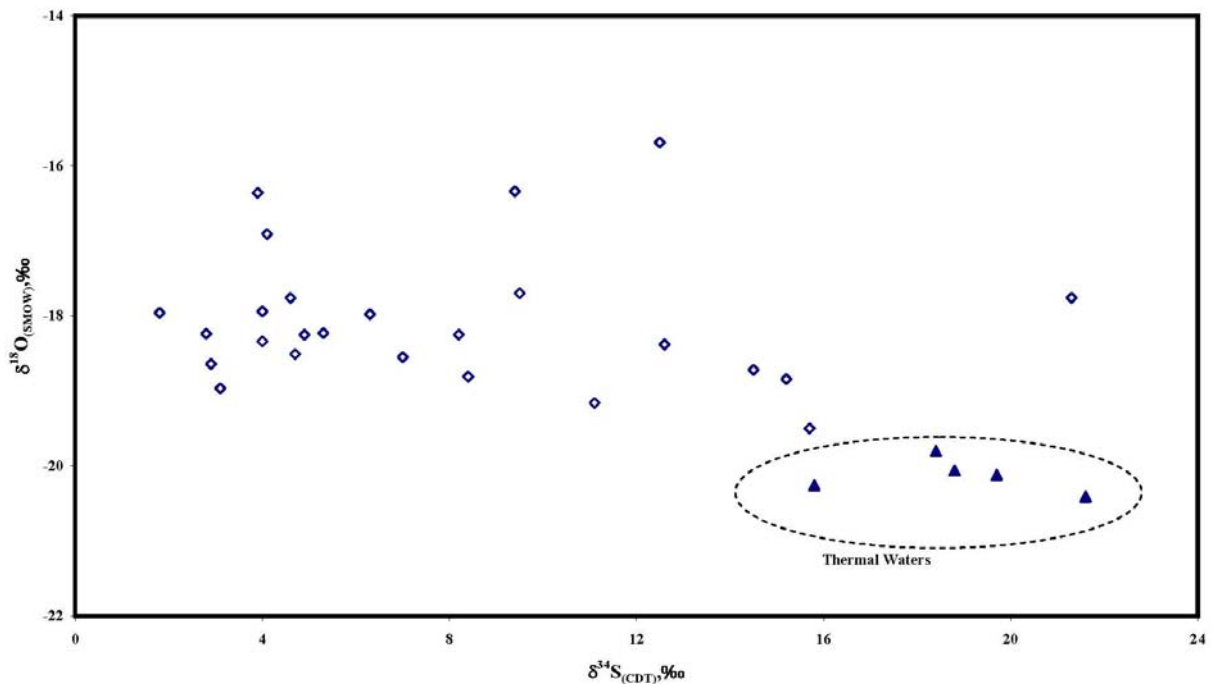


Figure 7: Plot of $\delta^{34}\text{S}_{\text{SO}_4}$ vs. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ in groundwater and geothermal water

Mine tailings and smelter wastes the southern Deer Lodge Valley are a mineral processing by-product of sulfide-rich ore from the Butte Mining District. Thus, the sulfur isotope composition of the sulfide minerals at Butte are an important baseline to which the sulfate in groundwater can be compared. Lange and Cheney (1971) analyzed 110 ore samples from Butte for sulfur isotope composition and reported a mean $\delta^{34}\text{S}$ value of 0.4‰ and standard deviation of 1.6‰ for all the samples analyzed.

Data Evaluation

A review of the available groundwater data indicate that sulfate concentrations above approximately 30 mg/L are elevated as a result of sulfate contributed from mine waste leachate or geothermal discharge. The dominant source of sulfate in groundwater at a particular location can be distinguished on the basis of the sulfur isotope composition for sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) and, to a lesser extent, the concentration of sodium. Water temperature may also be indicative of geothermal influences. $\delta^{34}\text{S}_{\text{SO}_4}$ values in groundwater reflect the isotopic composition of the sulfate source or sources and any isotope fractionation that occurs along the flow path. Oxidation of pyrite and other sulfide minerals contained in waste materials and the dissolution of evaporite minerals (gypsum and anhydrite) are the major sources of sulfate to groundwater in the southern Deer Lodge Valley.

Tailings within the Anaconda and Opportunity Ponds average approximately 4.4% total sulfur by weight, with pyritic sulfur (FeS_2) comprising more than 90% of the total sulfur (Tetra Tech, 1986). The range of $\delta^{34}\text{S}_\text{S}$ for all common sulfides in Butte ore range from -3.7 to +4.8‰ with a mean value of +0.4‰ (Lange and Cheney, 1971). Pyrite from Butte ore has a mean $\delta^{34}\text{S}$ value of +1.4‰ and ranges from +0.5 to +4.1 ‰. Sulfate generated from the oxidation of pyrite in waste materials in the southern Deer Lodge Valley should, therefore, have $\delta^{34}\text{S}$ values between roughly 0 and + 4‰.

The $\delta^{34}\text{S}_{\text{SO}_4}$ values for evaporitic rocks vary greatly and generally correspond to the geologic age of deposition. The $\delta^{34}\text{S}_{\text{SO}_4}$ values for geothermal water in the southern Deer Lodge Valley (+15.8 to +21.8‰) are consistent with the expected range of $\delta^{34}\text{S}_{\text{SO}_4}$ values for gypsum and anhydrite (+10 to +30‰) in Paleozoic deposits (Nielsen et al., 1991), which may be present at depth in the Anaconda-Pintlar and Flint Creek Ranges.

A plot of the $\delta^{34}\text{S}_{\text{SO}_4}$ against sulfate concentrations for groundwater and geothermal water samples is shown in Figure 8. The majority of the data plot between +0‰ and +5‰. These data reflect sulfate derived from reduced sulfur and suggest that leachate from tailings or other mining related wastes are the primary source of sulfate in the samples analyzed. Geothermal waters are highly enriched in ^{34}S relative to most groundwater samples and plot in an obvious group with $\delta^{34}\text{S}_{\text{SO}_4}$ values between +15.8 and +21.8‰. Data that are depleted in ^{34}S show a dilution trend whereby high sulfate waters are diluted by unimpacted waters along a flowpath away from the sulfate source (e.g., Opportunity Tailings Ponds). Data that plot between about +5‰ and +15‰ are indicative of either a mixture of sulfate from mine waste and thermal sources or isotope fractionation during sulfate reduction processes. The latter process would enrich residual sulfate in ^{34}S relative to the more reduced sulfur species.

Both sodium and sulfate concentrations are elevated in geothermal water whereas sodium concentrations are lower in groundwater impacted by mining-related wastes, particularly in the central portion of the valley down-gradient of the Opportunity Tailings

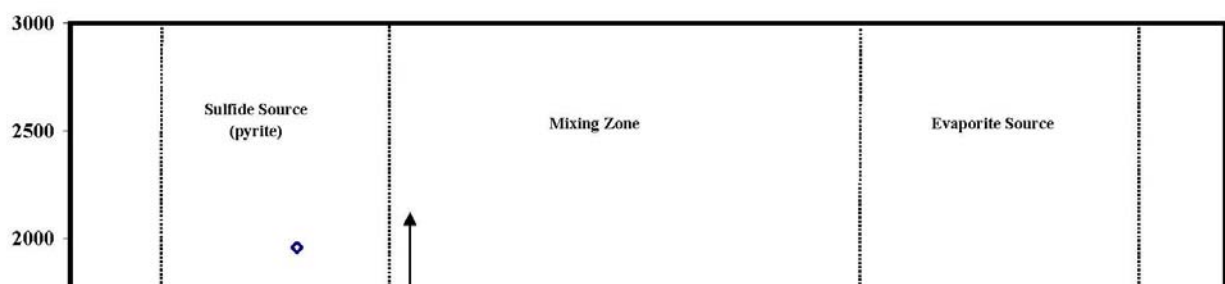
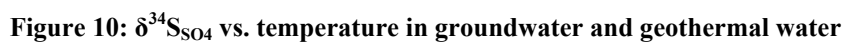
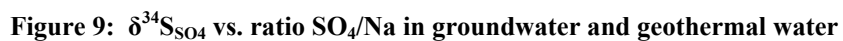


Figure 8: $\delta^{34}\text{S}_{\text{SO}_4}$ vs. SO_4 in groundwater and geothermal water

Ponds. A mixing trend is apparent between mine-waste-impacted groundwater with low $\delta^{34}\text{S}_{\text{SO}_4}$ and low sodium concentration to high $\delta^{34}\text{S}_{\text{SO}_4}$ and higher sodium percentage in geothermal water. To illustrate this relationship, $\delta^{34}\text{S}_{\text{SO}_4}$ is plotted against the ratio SO_4/Na in Figure 9.

Water temperature is an obvious indicator of geothermal water. Temperatures for geothermal water discharging at Fairmont Hot Springs and Warm Springs are 158 and 172°F, respectively. Groundwater temperatures measured from 124 monitoring wells in the study area ranged from 39.6 to 63.3°F and averaged 47.7°F. A plot of water temperature against $\delta^{34}\text{S}_{\text{SO}_4}$ is shown in Figure 10. Although there is considerable scatter in the data, groundwater samples with heavier isotope signatures generally have slightly higher temperature. Thus, wells with elevated groundwater temperatures are very likely influenced by geothermal discharge. Wells that have higher groundwater temperature and high $\delta^{34}\text{S}_{\text{SO}_4}$ values include Well 14, Well 15, Well 17, and C2BR. Well C2BR is located on Smelter Hill in the area of the fault and inactive geyser (SH HS). Wells 14, 15, and 17 are located in the southern portion of the study area in the vicinity of Fairmont Hot Springs. Groundwater temperature above 50°F is higher than normal groundwater temperatures for the area and is considered an indicator of possible geothermal influences.



Discussion

Evaluation of the stable isotope and solute chemistry for groundwater and geothermal water in the southern Deer Lodge Valley provides insight to the sources of the water and its chemical composition. Hydrogen and oxygen isotope compositions for geothermal water and groundwater indicate that both geothermal waters and groundwater are derived from atmospheric precipitation. Further, geothermal systems receive recharge from the high elevations in the surrounding mountains and direct precipitation in the valley is responsible for recharging the shallow alluvial system. Recharge from surrounding highland areas travels to depth through a network of fractures, faults, and/or fissures, is heated, and then is transmitted back to the surface along fault surfaces within the valley. Intersecting faults are interpreted to exist beneath Warm Springs and possibly Smelter Hill, and these fault intersections are thought to facilitate the upward migration of geothermal waters. Geothermal discharge at Fairmont Hot springs is controlled by fractures within the granitic rocks south, west, and potentially east of Gregson.

The similar calcium-sodium-sulfate signature of the geothermal waters at Warm Springs and Smelter Hill indicate that the recharge areas and flow paths to these springs are similar geologically and further suggest that the geothermal waters have chemically interacted with both calcareous and granitic/volcanic rocks. The calcium in these waters indicates interactions with calcareous rocks at depth. Limestone and other calcareous rocks are abundant in the Precambrian (Belt), Paleozoic, and Mesozoic sedimentary sequences of the Flint Creek and Anaconda-Pintlar Ranges (Wanek and Barclay, 1966). Topographic relations suggest recharge comes from the ranges to the west and these mountain ranges contain abundant limestone and calcareous rocks. The sodium in geothermal waters at Warm Springs and Smelter Hill is derived from granitic and/or volcanic rocks which comprise Smelter Hill and the floor of the southern Deer Lodge Valley. These feldspathic igneous rocks release sodium through the dissolution of Na-feldspar.

The source of sulfate in the Warm Springs and Smelter Hill geothermal waters is the product of gypsum or anhydrite dissolution. Regionally, the most significant evaporite units are contained within the Mississippian Charles Formation. The Charles Formation is a member of the Madison Group and consists of interbedded thick to thin beds of limestone and anhydrite (CaSO_4) (Seager, 1942). The Madison Group is exposed in a wide belt that crosses Lost Creek near its confluence with Timber Gulch also crops out in the Flint Creek Range north of Warm Springs Creek.

Dissolved solutes in the geothermal water discharging at Fairmont Hot Springs (FHS) also suggest geothermal water interaction with both granitic/volcanic rocks and sedimentary rocks along the flow path prior to discharge. However, the lower sulfate concentration and higher sodium concentration indicate a greater influence from granitic/volcanic rocks. Geothermal water discharging at Fairmont Hot Springs bears a sodium-sulfate-bicarbonate signature. The high sodium content at Fairmont Hot Springs (96.2% of the cation concentration) indicates that the dominant chemical influence on

this geothermal system is the granitic/volcanic rocks underlying Fairmont Hot Springs and in the mountains surrounding Gregson to the south, east, and west. Bicarbonate occurs as a result of a chemical reaction between meteoric water and dissolved carbon dioxide in surficial soils and with carbonate rocks. As described earlier for the Warm Springs and Smelter Hill geothermal system, evaporitic rocks in the western highlands are the probable source of sulfate to the geothermal system at Fairmont Hot Springs. Thus, throughout its circulatory route, geothermal water interacts with granitic/volcanic rocks and, to a lesser extent, evaporitic rocks prior to discharge at Fairmont Hot Springs.

The sulfur isotopic composition of sulfate indicates that dissolved sulfate is enriched in the heavy isotope of sulfur (^{34}S) in groundwater influenced by geothermal discharge relative to groundwater influenced by mine waste leachate. $\delta^{34}\text{S}_{\text{SO}_4}$ values for groundwater down-gradient of mine waste sources in the study area are generally between 2.0‰ and 5.0‰. $\delta^{34}\text{S}_{\text{SO}_4}$ values for geothermal waters in the southern Deer Lodge Valley range from 15.8‰ (Fairmont Hot Springs) to 21.8‰ (Warm Springs) which are indicative of an evaporitic source of sulfate consistent with the model for geothermal recharge described above. Groundwater samples with intermediate $\delta^{34}\text{S}_{\text{SO}_4}$ values (5.0 to 15.8‰) are indicative of sulfate derived from a mixture of mine waste leachate and geothermal sources or may reflect a different source of sulfate altogether.

All sulfate contributed to southern Deer Lodge Valley groundwater from either geothermal discharge or leaching of mine waste could not be accounted for entirely. Therefore, the percentage of the total sulfate in groundwater derived from geothermal discharge and leaching of mine wastes, respectively, were estimated by quantifying the magnitude of sulfate produced from the major geothermal and mine waste sources. The total combined mass of sulfate in surface discharge at Warm Springs, Fairmont Hot Springs, and Smelter Hill was compared to the total mass of sulfate derived from the Opportunity Ponds, Anaconda Ponds, Warm Springs Ponds, and floodplain tailings along Silver Bow Creek to quantify the relative magnitude of the total sulfate production that can be attributed to geothermal discharge. A discussion of the assumptions made in performing these calculations is presented below. The results of the evaluation are shown in Table 2.

All together, the Opportunity, Anaconda, and Warm Springs Ponds, and the floodplain tailings along Silver Bow Creek are responsible for contributing approximately 37,800 lbs/day of sulfate to the shallow alluvial groundwater system in the southern Deer Lodge Valley. The sulfate load that is discharged from geothermal springs in the southern Deer Lodge Valley totals 541 lbs/day. Combining the sulfate load from the mine waste sources with the total sulfate discharged in the thermal springs produces 38,341 lbs/day sulfate, 98.6 percent of which can be attributed to mine waste discharge and 1.4 percent to geothermal discharge.

Table 2. Sulfate loading to groundwater from known geothermal and mine-waste sources in the southern Deer Lodge Valley, Montana

Source of Sulfate	Sulfate Concentration (mg/L)	Discharge (liters/min)	Sulfate Concentration (lbs/ft3)	Discharge (ft3/sec)	Discharge (ft3/day)	Sulfate Loading (lbs/day)
Thermal Discharge						
Warm Springs	560	230	0.035	0.135	11,696	408
Fairmont Hot Springs	180	150	0.011	0.088	7,628	86
Inactive Geyser on Smelter Hill	1,360	11	0.085	0.006	559	47
Total:						541
Mine Waste Discharge						
<i>Vertical Leakage (Vadose Zone)</i>						
Opportunity Ponds	5,000	968	0.311	0.570	49,248	15,338
Anaconda Ponds	1,420	306	0.088	0.180	15,552	1,376
Warm Springs Ponds	1,125	5,301	0.070	3.120	269,568	18,890
Tailings Along Silver Bow Ck.	1,364	477	0.085	0.281	24,278	2,063
<i>Horizontal Throughflow (Phreatic Zone)</i>						
Opportunity Ponds	1,855	3.4	0.116	0.002	173	20
Anaconda Ponds	758	12	0.047	0.007	605	29
Total:						37,716
Total Sulfate Loading (Lbs./day)						
						38,256
% Sulfate From Thermal Water						1.4%
% Sulfate From Mine Wastes						98.6%

Recognizing that the discharge of geothermal water from the springs at Warm Springs, Fairmont Hot Springs, and Smelter Hill does not account for any subsurface geothermal discharge, additional sulfate loading from geothermal discharge at depth must be considered. It is highly probable that equilibrium discharge from geothermal systems in the southern Deer Lodge Valley are no more than one order of magnitude greater than the surface discharge at the respective spring locations. Thus, increasing the magnitude of sulfate loading from geothermal discharge by a factor of 10 yields 5,410 lbs/day sulfate from a non-mining related source. This is considered to be the upper limit for geothermally derived sulfate in the southern Deer Lodge Valley. At this level of input, geothermal discharge would account for 14 percent of the total sulfate loading to groundwater in the southern Deer Lodge Valley. Much of this sulfate however, would likely not be seen in the shallow aquifer because of the great depths to the valley floor throughout much of the basin. Also, other smaller mine waste sources (e.g., contaminated soils on Smelter Hill, the Yellow Ditch, and the Blue Lagoon) were not considered in the above analysis. Additional sulfate from smaller mine waste sources would result in a lower total percentage of the sulfate observed in the shallow alluvial aquifer. It is therefore reasonable to assume that at least 90 percent and perhaps more of the elevated sulfate concentrations observed in groundwater in the southern Deer Lodge valley may be attributed to leachate from sulfidic mine wastes. This conclusion is consistent with the interpretation of sulfur isotope data. Isotopic data evaluated for groundwater samples collected in the southern Deer Lodge Valley predominantly indicate a sulfide source for the sulfate in groundwater.

Conclusions

Evaluation of stable isotope and solute chemistry has lead to the following conclusions regarding shallow groundwater in the southern Deer Lodge Valley:

- Water that discharges from geothermal springs located at Warm Springs, Fairmont Hot Springs, and Smelter Hill is depleted in the heavy isotope of oxygen (^{18}O) relative to area groundwater;
- Geothermal water is meteoric in origin;
- Geothermal systems are recharged at high elevations in the mountains surrounding the valley. The chemistry of geothermal water is influenced by chemical interaction with rocks and sediments along its flow path;
- Structural features in the valley, including basin forming faults and bedrock fractures, control the flow and distribution of geothermal water. The location of geothermal springs may be a result of intersecting faults at depth;
- Geothermal water is enriched in the heavy isotope of sulfur ($\delta^{34}\text{S}_{\text{SO}_4}=15.8 - 21.8\text{‰}$), indicative of an evaporitic source;
- Sulfur isotope values for mine waste leachate ($\delta^{34}\text{S}_{\text{SO}_4}\approx 2 - 5\text{‰}$) correlate well with the average $\delta^{34}\text{S}_{\text{SO}_4}$ values for pyrite in the Butte ore deposit;
- Influences on shallow groundwater from geothermal discharge are not widespread;

- A linear mixing trend is apparent in groundwater for sulfate derived from geothermal discharge and sulfate derived from mine waste leachate.
- Sulfate derived from geothermal discharge is masked by widely distributed sulfate from leaching mine wastes. It is estimated that less than 10 percent of the total mass of sulfate in the shallow groundwater system is derived from geothermal discharge.

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